

## REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

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AD-A263 728



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## 2. REPORT DATE

3/24/93

## 3. REPORT TYPE AND DATES COVERED

Final 1 Sep 89 - 31 Dec 92

## 4. TITLE AND SUBTITLE

Characterization of Lithium Electrode Surface in Lithium Secondary Batteries by In Situ Raman Spectroscopic Methods

## 5. FUNDING NUMBERS

DAA03-89-G-0105

## 6. AUTHOR(S)

Hiroyasu Tachikawa

## 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Jackson State University  
1400 Lynch Street  
Jackson, MS 39217

## 8. PERFORMING ORGANIZATION REPORT NUMBER

## 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U. S. Army Research Office  
P. O. Box 12211  
Research Triangle Park, NC 27709-2211

## 10. SPONSORING/MONITORING AGENCY REPORT NUMBER

ARO 27241.1-CH-SAH

## 11. SUPPLEMENTARY NOTES

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## 12a. DISTRIBUTION/AVAILABILITY STATEMENT

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## 12b. DISTRIBUTION CODE

## 13. ABSTRACT (Maximum 200 words)

Surface layers on lithium electrodes formed in several solvents including dimethyl carbonate (DMC), diethyl carbonate (DEC), polyethylene glycol 400 dimethyl ether (PEG400DME), and propylene carbonate (PC) have been studied by Raman spectroscopy. Both DMC and DEC were used singly, and also mixed with either methyl acetate or methyl formate. The Raman spectra showed that passive films formed on the Li surface in different solvents may have different chemical structures, which changed during the charging and discharging processes. A solid film of fullerene  $C_{60}$ , which could be used as a cathode in Li rechargeable batteries, was examined in the PEG400DME solution by both electrochemical and Raman spectroscopy. Cyclic voltammograms (CVs) showed five redox peaks which suggested the formation of  $C_{60}^-$ ,  $C_{60}^{2-}$ ,  $C_{60}^{3-}$ ,  $C_{60}^{4-}$ , and  $C_{60}^{5-}$ . Raman spectra obtained from thin  $C_{60}$  film indicated that the thin fulleride film dissolved in the PEG400DME/ $LiClO_4$  solution at negative potentials.

## 14. SUBJECT TERMS

lithium electrode, fullerenes, electrochemistry,  
Raman spectroscopy

## 15. NUMBER OF PAGES

20

## 16. PRICE CODE

## 17. SECURITY CLASSIFICATION OF REPORT

UNCLASSIFIED

## 18. SECURITY CLASSIFICATION OF THIS PAGE

UNCLASSIFIED

## 19. SECURITY CLASSIFICATION OF ABSTRACT

UNCLASSIFIED

## 20. LIMITATION OF ABSTRACT

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CHARACTERIZATION OF LITHIUM ELECTRODE SURFACE  
IN LITHIUM SECONDARY BATTERIES BY IN SITU  
RAMAN SPECTROSCOPIC METHODS

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FINAL REPORT

BY

HIROYASU TACHIKAWA

MARCH 24, 1993

Accession For	
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9 3 5 0 4 1 8 9

93-09572



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#### **A. The problem studied.**

Surface layers on lithium electrodes in different solvents including propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and polyethylene glycol 400 dimethyl ether (PEG400DME) have been characterized by using Raman spectroscopy. Both DMC and DEC were used singly, and also mixed with either methyl acetate (MA) or methyl formate (MF) in order to study the effects of solvent on the lithium surface. Raman spectroscopy was also used to study the structural change of surface layers on lithium electrode during the charging and discharging processes.

A couple of materials including a solid film of fullerenes ( $C_{60}$  and  $C_{70}$ ) and polymetallophthalocyanine thin films have been studied by both electrochemical methods and Raman spectroscopy. These materials could be used as a cathode in Li secondary batteries.

#### **B. Summary of results.**

**Li electrode in DMC, DEC, and mixed solvents with MA and MF.** Raman spectroscopy was carried out at a silver electrode surface after depositing thin lithium films (50, 150, 250, 350, 500, and 1000 Å) in dimethyl carbonate (DMC) solution with 1.0 M  $LiClO_4$ . A conventional two-compartment cell was used, and the solution was transferred from the cell compartment to the reservoir before recording the Raman spectra. An  $Ar^+$  laser was used as the excitation source. Strong Raman signals appeared after 50 Å lithium film was deposited on silver by reduction of  $Li^+$  in the solution. The intensity of Raman bands decreased sharply after 100 Å lithium film was deposited. The potential of the working electrode shifted from positive (0.2 V) at the start of deposition to negative (-0.48 V) after depositing 50 Å of Li. Several Raman bands from DMC and  $LiClO_4$  were observed

in the spectra recorded after deposition of 50-1000 Å Li films. Several bands (154, 348, 449, and 610  $\text{cm}^{-1}$ ) unrelated to the solution species were observed in the low frequency region after deposition of 50 Å Li (see Figure 1). These bands disappeared when thicker lithium films (100 and 500 Å) were deposited. Several broad high intensity bands (1502, 1559, and 1583  $\text{cm}^{-1}$ ) appeared after deposition of 350 Å lithium (see Figure 2). Basically, the same spectrum was observed after depositing 500 and 1000 Å lithium films. The potential of the working electrode shifted from 0.6 V to -0.3 V during deposition of the 150 Å Li film. However, the potential of the working electrode remained positive when thicker lithium films (250-1000 Å) were deposited. The Raman results and the potential changes observed during lithium deposition suggested that the lithium film is stable in DMC/ $\text{LiClO}_4$  solution. The strong Raman scatterings, which were observed after deposition of 50 Å Li, may be due to the surface-enhanced Raman signal. The negative potential (-0.48 V) observed just after deposition of the 50 Å film also indicated that the Li film remained briefly on the silver electrode surface. The low Raman intensity and the positive electrode potential after deposition of thicker films suggested that the lithium film reacted with the solvent and formed a reaction product. It is likely that the reaction product on the surface of the silver electrode reacted with lithium which was on the surface of the silver electrode. The broad Raman bands in the high frequency range (1502, 1559, and 1583  $\text{cm}^{-1}$ ) (see Figure 2) may be due to the reaction product of Li and DMC. On the other hand, several low frequency bands observed after deposition of 50 Å Li could be due to a passivating film on the lithium surface.

Contrary to the results obtained in the DMC solution, no significant Raman bands were observed at the smooth Ag electrode after depositing Li in DEC solution. The surface

of the Ag electrode looked unchanged after deposition of a 500 Å Li film. The absence of Raman scatterings at the silver surface in the DEC solution may be due to the immediate reaction between Li and DEC. The color of the clear  $\text{LiClO}_4/\text{DEC}$  solution changed to brown after deposition of the Li films, and the brown color intensified as thicker Li films were deposited. No significant Raman bands were observed on the surface of the anodized silver after deposition of Li films (50-2000 Å). However, a broad strong luminescence band appeared in the 1200-1700  $\text{cm}^{-1}$  range after Li deposition. The result suggested that the cathodically deposited Li film reacted with DEC to form decomposition products which are responsible for the observed strong luminescence.

The stability of lithium in DEC solution was also studied in the presence of methyl formate (MF) by using Raman spectroscopy. The ratio of DEC and MF was 1 to 1, and 1 M  $\text{LiClO}_4$  was used as a supporting electrolyte. Raman spectra were recorded at a smooth silver electrode (3000 Å thick) after depositing Li films (50, 100, 200, 350, 500, 1000, and 2000 Å) by constant current electrolysis. Raman spectra (100-1700  $\text{cm}^{-1}$  range), which were recorded after deposition of Li films, did not show any significant bands. Also, the surface of the silver electrode looked shiny during deposition of lithium films. The results suggested that the deposited Li thin film reacted with the solvent and then the reaction product immediately dissolved in the solution. White particles were formed in the solution during the Raman experiment. The results indicated that the lithium surface was more stable in mixed solvent of DEC and MF than in DEC. The white substance, which was formed during Li deposition, seemed to protect the Li surface. However, we could not characterize the white substance due to the lack of any significant Raman and fluorescence bands in the 100-1700  $\text{cm}^{-1}$  spectrum range.

**Li electrode in polyelectrolytes.** The cyclic voltammetric behavior of lithium electrodes in polyethylene glycol 400 dimethyl ether (PEG400DME) with  $\text{LiClO}_4$  (0.6 M) was investigated in an air-tight electrochemical cell filled with high purity argon gas. Thin-film silver (3000 Å thick) on a 1" x 1" x 1/16" glass plate was used as a working electrode, and lithium ribbon was used as both reference and auxiliary electrodes. A high cathodic current for the reduction of  $\text{Li}^+$  to Li started at  $\sim 0$  V when the potential was scanned from positive to negative. There was another low cathodic current which showed a peak near +0.6 V. An anodic peak current at +0.9 V as well as an anodic current with a shoulder at +0.5 V were observed. It was also observed that the lithium metal surface was stable in the PEG400DME.

Raman spectroscopy was carried out by using the same electrochemical cell. Either  $\text{Ar}^+$  laser (514.5 nm line) or  $\text{Kr}^+$  laser (647.1 nm line) was used as the excitation source. When the  $\text{Ar}^+$  laser was used as the excitation source, a strong broad luminescence appeared, and no significant Raman bands were observed. In-situ Raman spectra were recorded in the range between  $150\text{ cm}^{-1}$  and  $1700\text{ cm}^{-1}$ . The potentials applied to the silver electrode were between 3.0 V and -0.3 V. There were bands which were due to PEG400DME and  $\text{ClO}_4^-$  at all potentials (see Figure 3): 790, 804, 842, 1026, 1132, 1234, 1383, 1446, and  $1471\text{ cm}^{-1}$  for the PEG400DME; and  $929\text{ cm}^{-1}$  for  $\text{ClO}_4^-$ . Several bands including 247, 299, 346, 602, 635, 688, 719, 994, 1086, 1367, 1531, and  $1613\text{ cm}^{-1}$  were observed at -0.1 V, as shown in Figure 4 (only 500-900  $\text{cm}^{-1}$  range is shown). These bands are unrelated to the solution species and were observed even when the potential was increased to 3.0 V. The results suggested that the above Raman bands may be due to a passive film which formed during lithium deposition on the silver electrode. The results also



suggested that the passive film remained on the silver surface when the potential was reversed and moved to very positive potentials.

**Li electrode in propylene carbonate.** In-situ Raman spectroscopy of the lithium surface during the charging and discharging processes in propylene carbonated (PC) solution with  $\text{LiClO}_4$  was carried out with a  $\text{Kr}^+$  laser. The Raman spectra were recorded in the range between 150 and  $1700\text{ cm}^{-1}$ . The formation of a passive film on the lithium surface could be seen during the charging process. The Raman spectra obtained in the PC solution with 1.0 M  $\text{LiClO}_4$  at -1.0 V vs Li showed several Raman bands ( $1214$ ,  $1298$ , and  $1549\text{ cm}^{-1}$  etc) which are unrelated to the solution species; some of these Raman bands remained during the discharging process (potential was moved to 0.3 V and then to 1.0 V). When the charging and discharging processes were repeated several times, the Raman spectra gradually changed. A typical example is the observation of a  $1240\text{ cm}^{-1}$  band during the first charging process. The intensity of this band gradually decreased as the potential was changed to 0.3 and then to 1.0 V. A new band appeared at  $1255\text{ cm}^{-1}$  during the potential cycle. The results suggested that the structure of the passive film may have changed during the repeated charging and discharging processes.

**$\text{C}_{60}$  film electrode in polyethylene glycol 400 dimethyl ether.** A  $\text{C}_{60}$  thin film was prepared on a glassy carbon (GC) electrode surface. A linear sweep voltammogram showed five reduction peaks which suggested the formation of  $\text{C}_{60}^-$ ,  $\text{C}_{60}^{2-}$ ,  $\text{C}_{60}^{3-}$ ,  $\text{C}_{60}^{4-}$ , and  $\text{C}_{60}^{5-}$  (see Figure 5). The  $\text{C}_{60}$  did not dissolve in PEG400DME with  $\text{LiClO}_4$ . However,  $\text{C}_{60}$  anions could be dissolved in the above solvent.

The AC impedance measurements showed that the solution resistance of PEG400DME was about 100 times higher than that of an aqueous solution. This high

solution resistance caused large peak-to-peak separations of the  $C_{60}$  redox reactions. In order to overcome this problem, CVs were recorded by using a GC microelectrode which helped to reduce the peak potential shift to a few mV (see Figure 6). The redox current for the  $C_{60}/C_{60}^-$  pair was approximately twice as large as that for other redox pairs including  $C_{60}^{2-}$ ,  $C_{60}^{3-}$ ,  $C_{60}^{4-}$ , and  $C_{60}^{5-}$ . Other supporting electrolytes such as  $KClO_4$  and  $NaClO_4$  were also used to investigate the electrochemical behavior of  $C_{60}$  in the PEG400DME. Of these three alkaline metal salt electrolytes, the  $C_{60}$  anions were most stable with  $KClO_4$ .

Raman spectroscopy of the  $C_{60}$  film was carried out by using a  $Kr^+$  laser (647.1 nm) as the excitation source. A thin  $C_{60}$  film deposited on a thin-film silver electrode surface was placed in an air-tight electrochemical cell filled with Ar gas, and Raman spectra were recorded using the back scattering mode. Several medium-to-strong Raman bands due to solid  $C_{60}$  were observed at 273-1566  $cm^{-1}$  at the open circuit potential. The above results are consistent with that of a  $C_{60}$  film prepared in vacuum.<sup>2</sup> We found it difficult to observe the Raman spectra of  $C_{60}$  anions because the  $C_{60}$  films dissolved in PEG400DME/ $LiClO_4$  solution when a negative potential was applied to the electrodes.

**Polymetallophthalocyanine film electrodes.** Polymetallophthalocyanines (PMePc) with three different metal centers including Ni, Co, and Cu were electrochemically prepared on the glassy carbon (GC) electrode. All the thin PMePc films (less than 30 nm) showed the catalytic reduction of  $O_2$  in the pH 7.4 phosphate buffer (PB) solution. The cyclic voltammetry (CV) showed three redox pairs for both PNiPc and PCuPc and four redox pairs for PCoPc in the potential range 0.6 to -1.0 V, as shown in Figure 7. In order to assign these redox pairs, both UV-visible and Raman spectroscopies were carried out. The UV-visible spectrum of PMePc film (~300 nm thick) deposited on indium tin oxide (ITO)

coated glass showed basically two changes when the potential was moved from 0.5 to  $-1.2$  V. The first change occurred near  $-0.2$  V where the second reduction of metal center took place; in the case of PCoPc (see Figure 8A), Co(II) was reduced to Co(I) at this potential. The second change accompanying the decreased absorption peak near 720 nm (see Figure 8B) was due to the reduction of ligand portion of the PCoPc film. This change may be related to the redox pair 4/4' in the CV (see Figure 7C).

In-situ Raman spectra of the PCoPc film in the air saturated PB (pH 7.4) solution (see Figure 9) indicated that a significant structural change of the PCoPc took place when the potential was stepped from 0.15 V to  $-0.1$  V and then to  $-0.4$  V: several new bands appeared at 680, 1422, 1606, and  $1716\text{ cm}^{-1}$ ; and a couple of bands at 1106 and  $1460\text{ cm}^{-1}$  showed a reduced intensity. These spectrum changes were not observed in the deaerated solution. The results may be associated with the formation of a complex species between PCoPc and  $\text{O}_2$ , which is related to the catalytic reduction of  $\text{O}_2$  at the PCoPc film electrode. The CV data at a thin (30 nm) PCoPc film showed a significantly increased catalytic current for the reduction of  $\text{O}_2$  near 0 V, which is parallel to the observed Raman spectrum changes in the same potential change.

C. List of all publications and technical reports.

"Raman spectroscopy of Lithium Electrode Surface", H. Tachikawa, C.S. Choi, and Z. Sun, Pittcon'91, Abstract No. 349 (1991).

"Electrochemical Behavior of Fullerene  $\text{C}_{60}$  Film Modified Electrode in Polyethylene Glycol 400 Dimethyl Ether", Z. Sun and H. Tachikawa, to be submitted to *J. Electrochem. Soc.*

**D. List of all participating scientific personnel.**

Research Associate: Zhisheng Sun

Graduate Students: Murari Rao, MS degree, May 1991

Hong H. Ge, Scheduled to obtain MS degree, June 1993

**Report of inventions**

None

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1. A.H.L. Goff, S. Joiret, B. Saidani, and R. Wiart, *J. Electroanal. Chem.* 253, 127 (1989).
2. D. Bethune, G. Meijer, N. Tang, and H. Rosen, *Chem. Phys. Letters*, 174, 219 (1990).

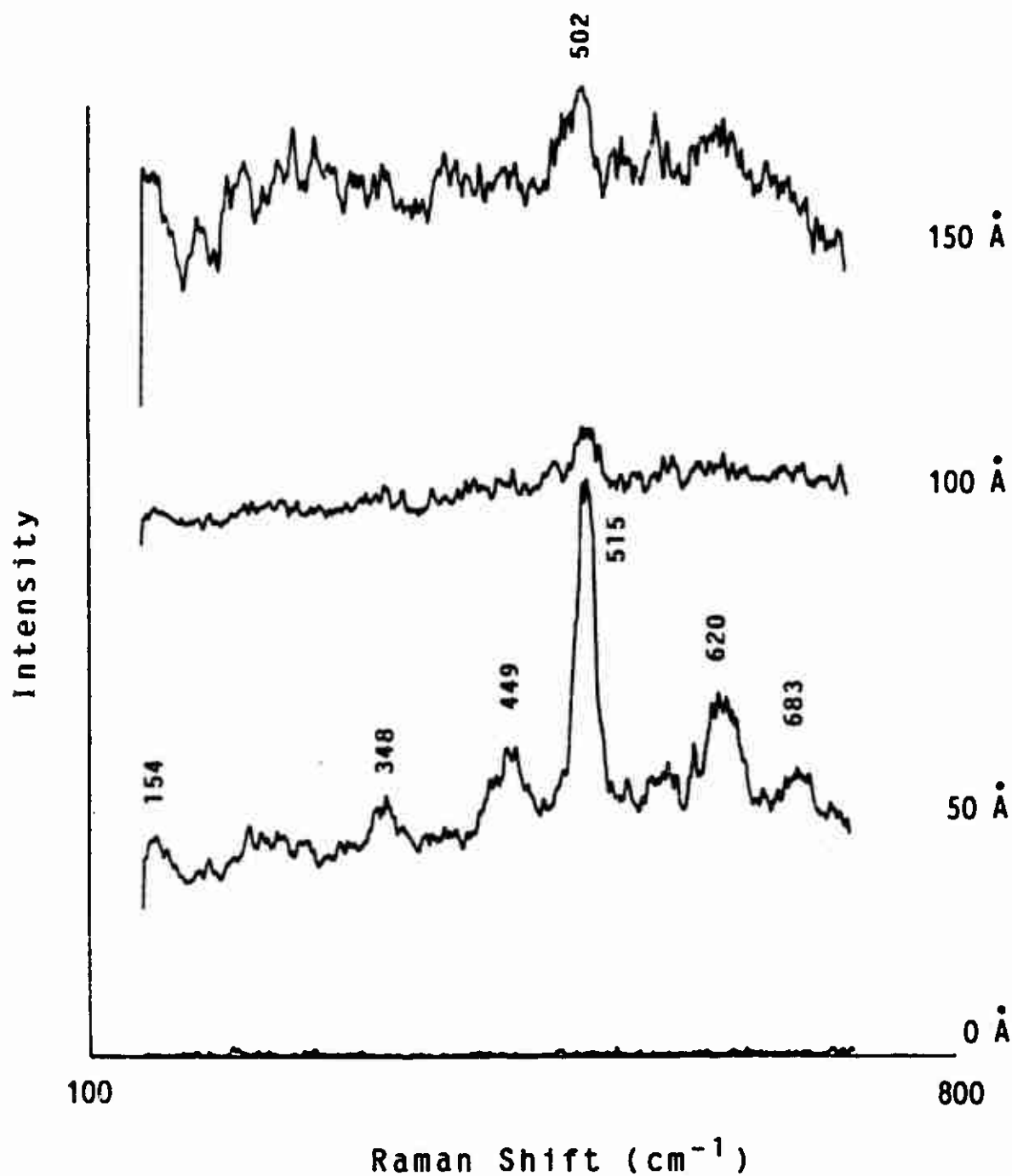


Figure 1a. Raman spectra ( $100\text{-}800\text{ cm}^{-1}$  region) at thin film Ag electrode after deposition of Li films in DMC/1 M  $\text{LiClO}_4$ ,  $\lambda_{\text{ex}} = 514.5\text{ nm}$  - 150 mW

Intensity

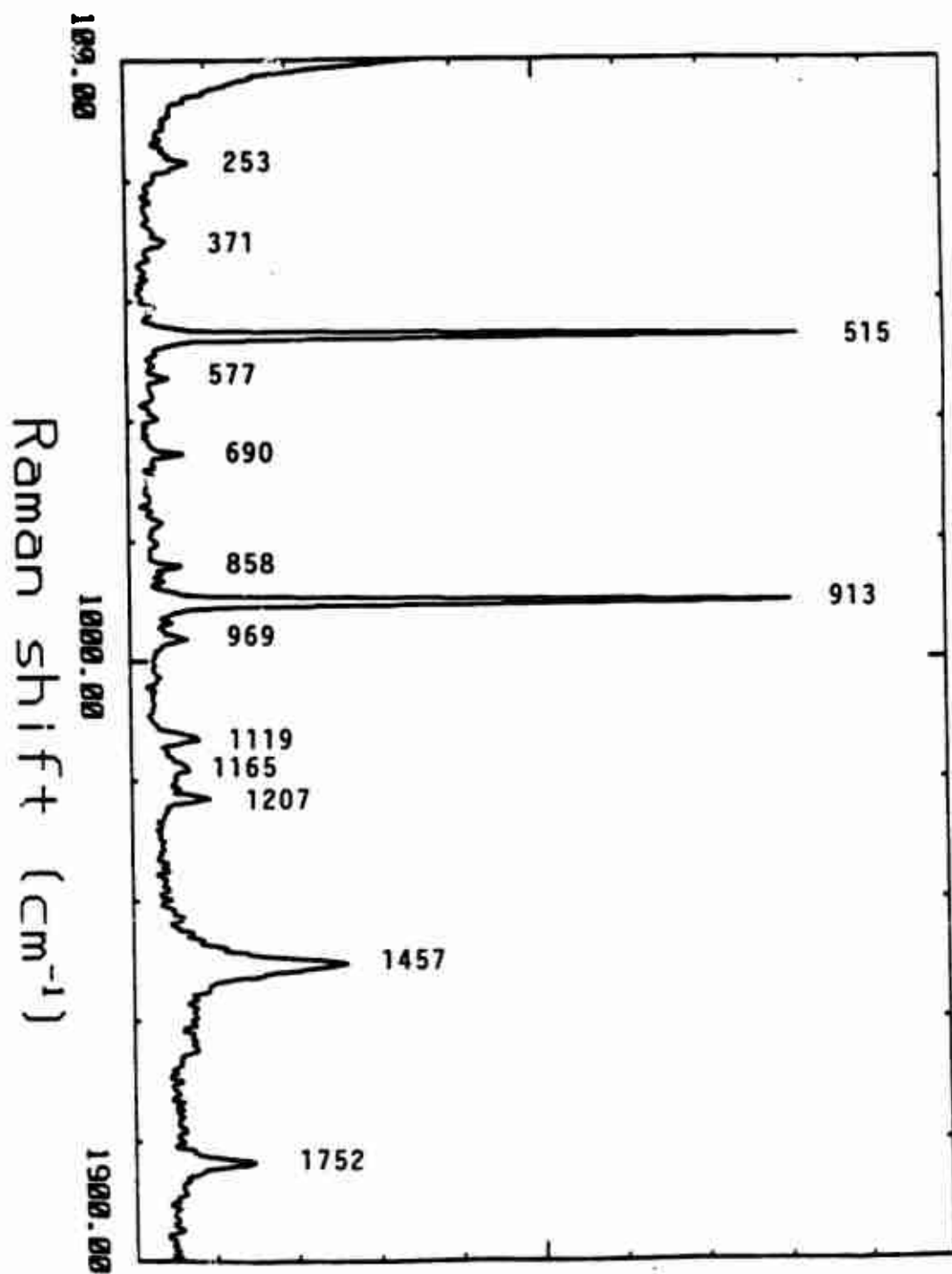


Figure 1b. Raman spectrum of DMC in quartz tube.  $\lambda_{\text{ex}} = 514.5 \text{ nm} - 150 \text{ nm}$

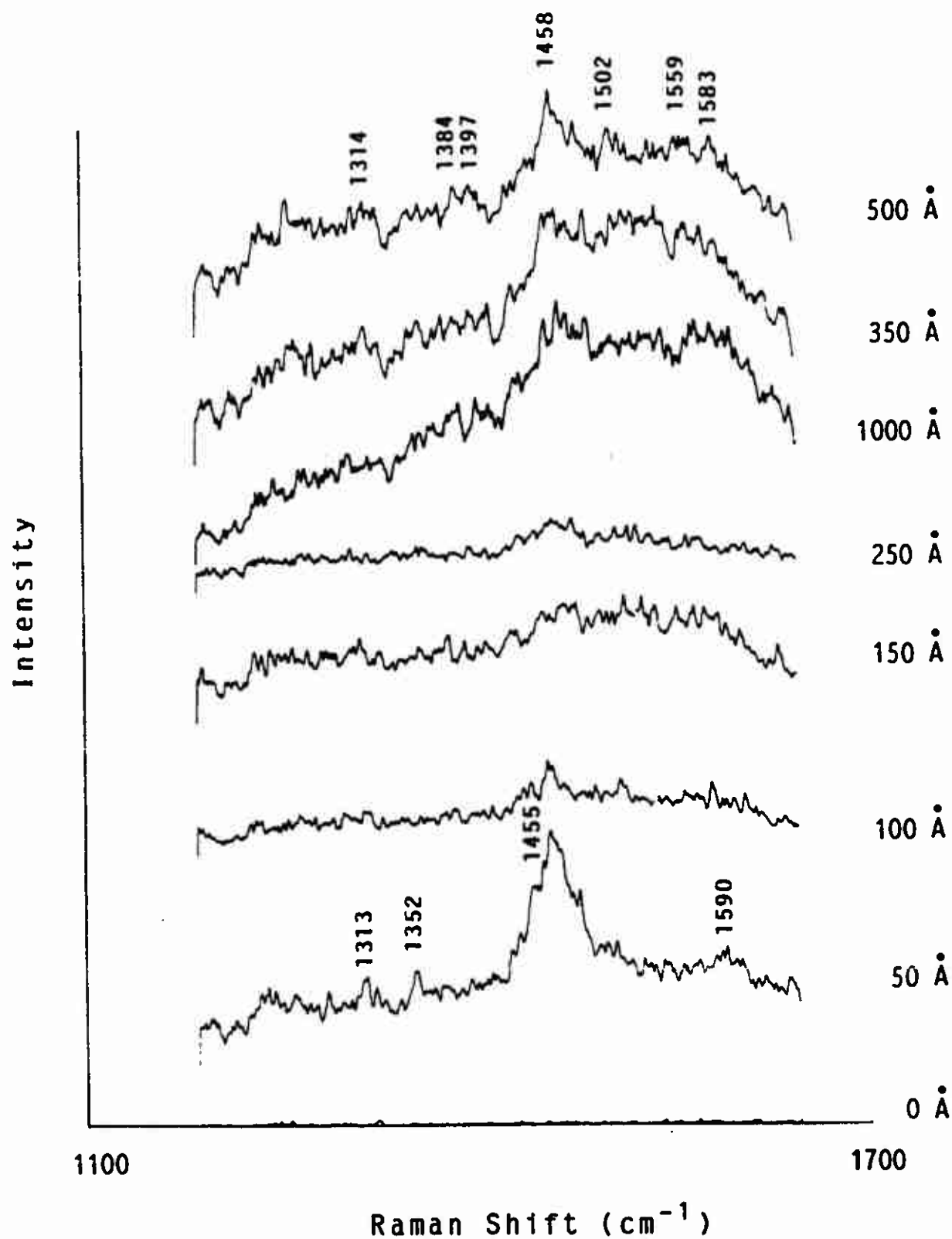


Figure 2. Raman spectra (1100-1700 cm<sup>-1</sup> region) of thin film Ag after the deposition of Li films in DMC/1M LiClO<sub>4</sub>.  
 $\lambda_{\text{ex}} = 514.5 \text{ nm} - 150 \text{ mW}$

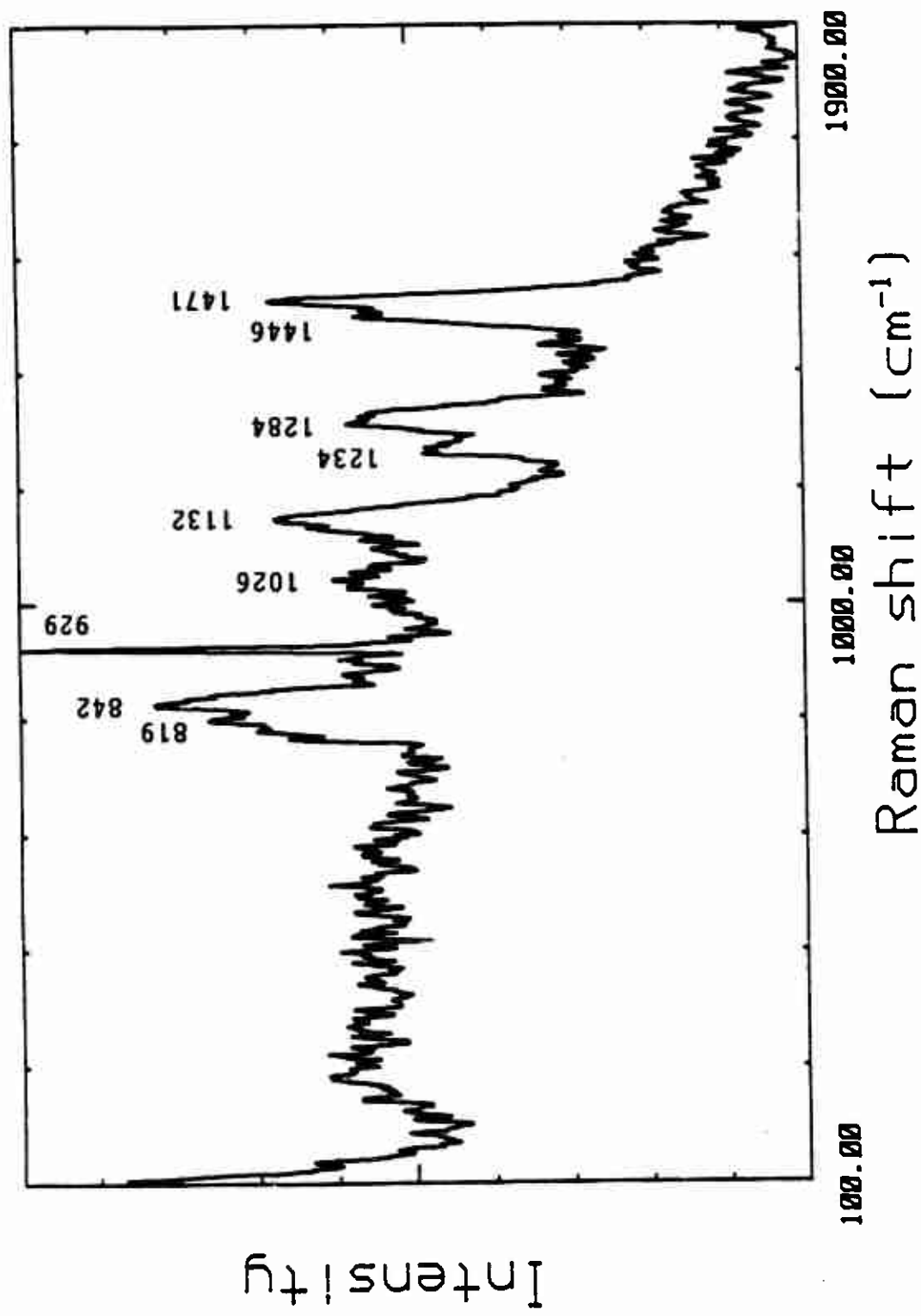


Figure 3. Raman spectrum (100-1900  $\text{cm}^{-1}$  range) of thin film Ag in PEG400DME/0.5 M  $\text{LiClO}_4$ . No potential was applied to the electrode.  $\lambda_{\text{ex}} = 647.1 \text{ nm}$  - 150 mW



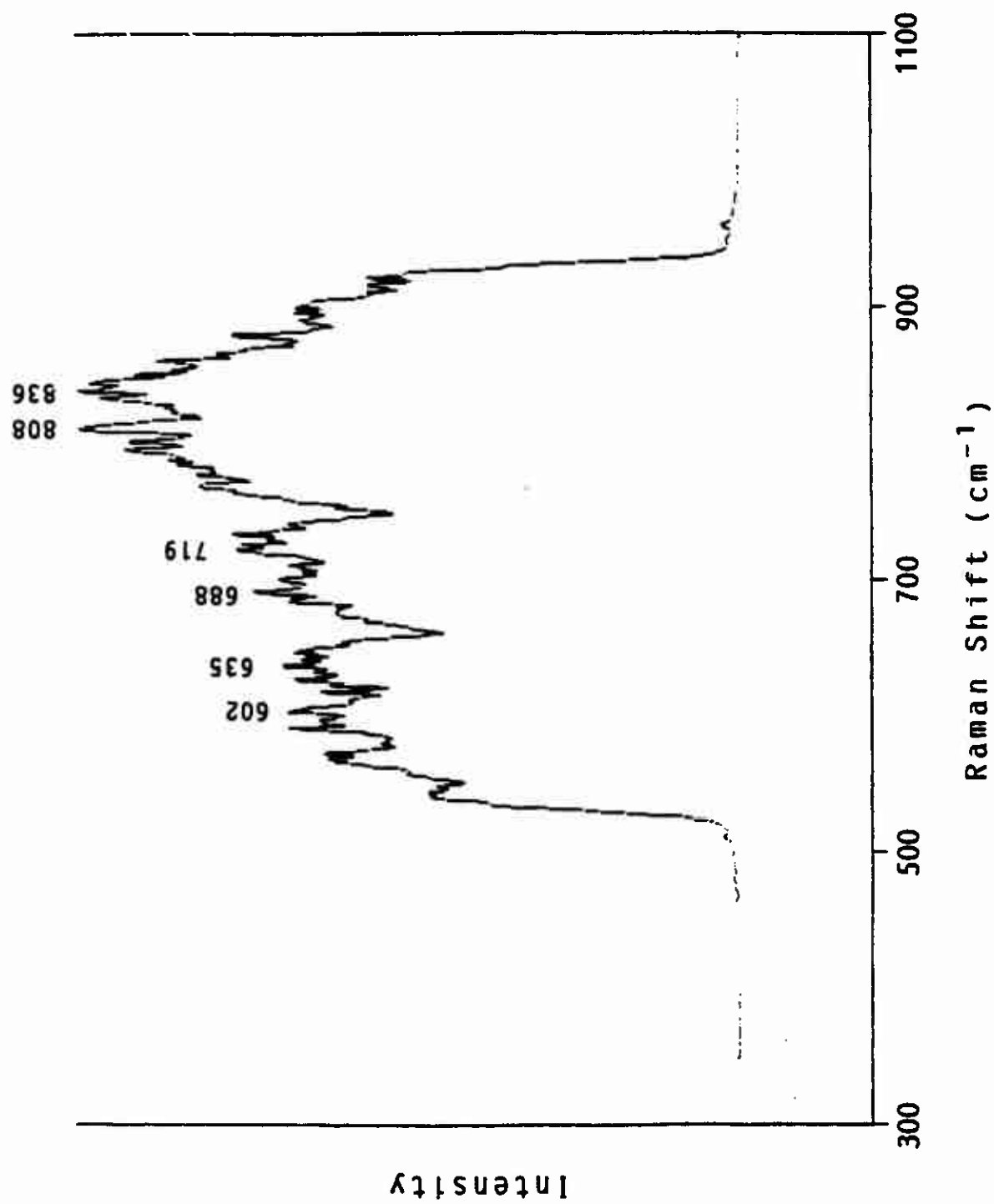


Figure 4. Raman spectrum (500-900 cm<sup>-1</sup> range) of thin film Ag at -0.1 V (vs Li<sup>+</sup>/Li) in PEG400DME/0.5 M LiClO<sub>4</sub>.  $\lambda_{ex} = 647.1$  nm - 150 mW

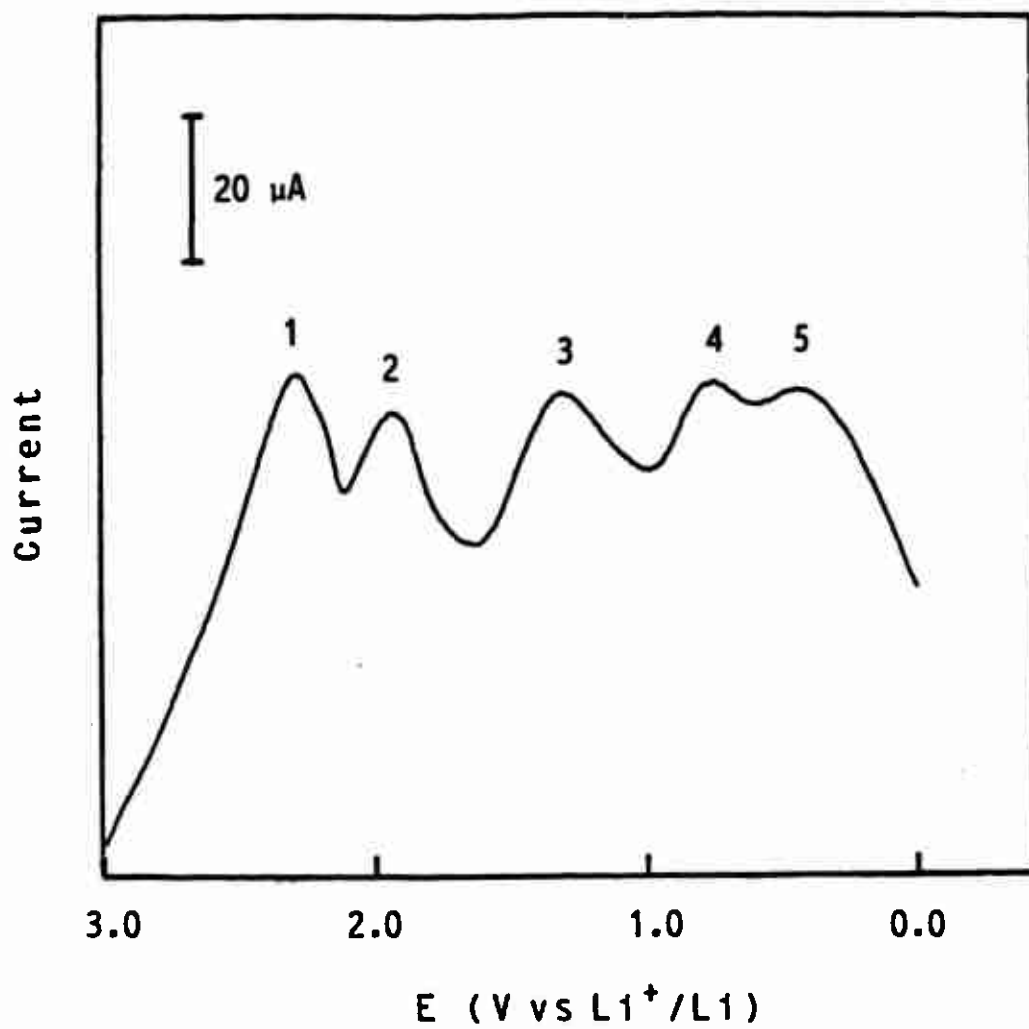


Figure 5. Linear sweep voltammogram at thin film  $\text{C}_{60}$  film on GC (3 mm dia) in PEG400DME/0.5 M  $\text{LiClO}_4$ . Scan rate: 100 mV/s

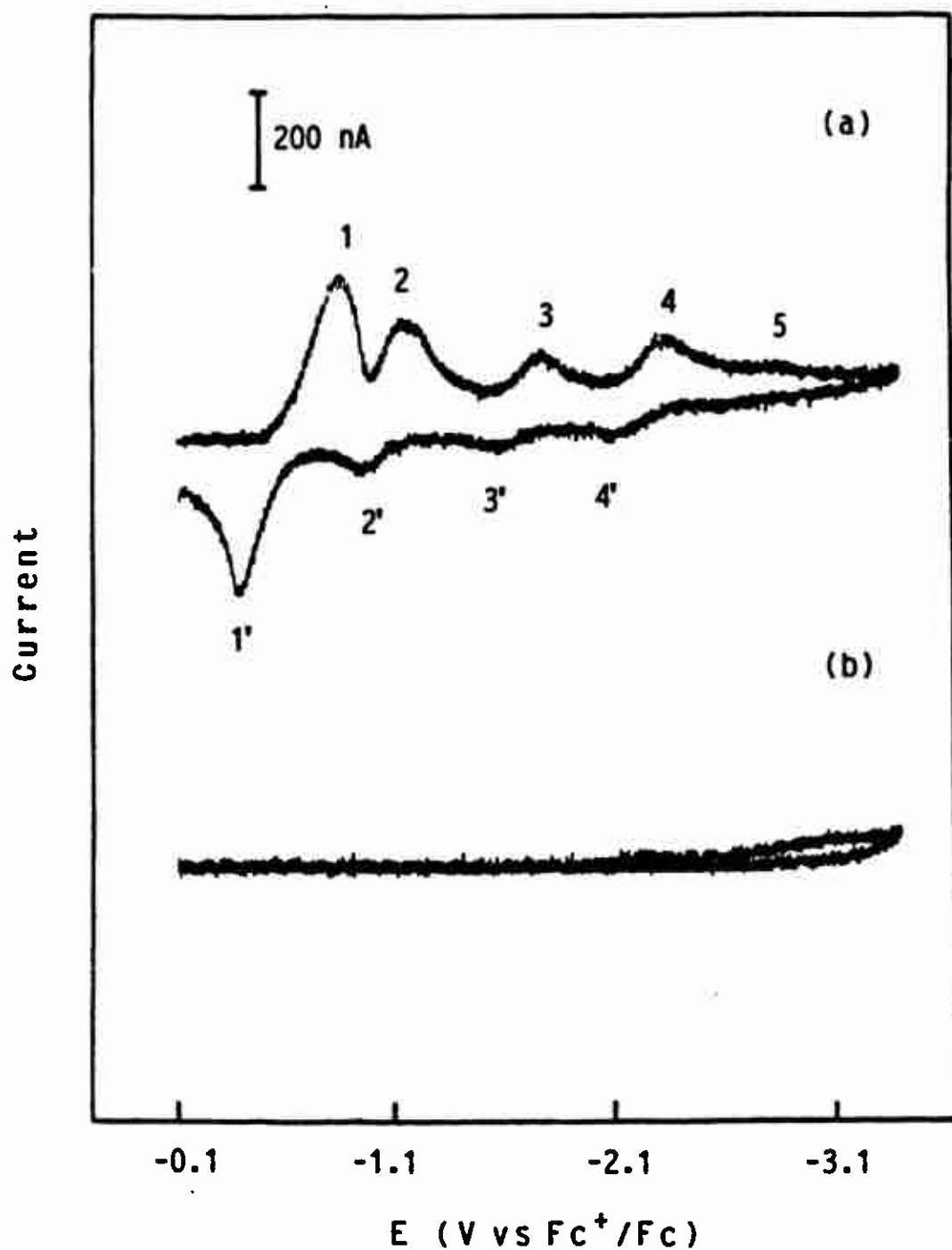


Figure 6. Cyclic voltammograms in PEG400DME/0.5 M  $\text{LiClO}_4$  at (a) thin  $\text{C}_{60}$  film on GC (30  $\mu\text{m}$ ) electrode and (b) on bare GC ( $\mu\text{m}$ ) electrode. Scan rate: 1 V/s

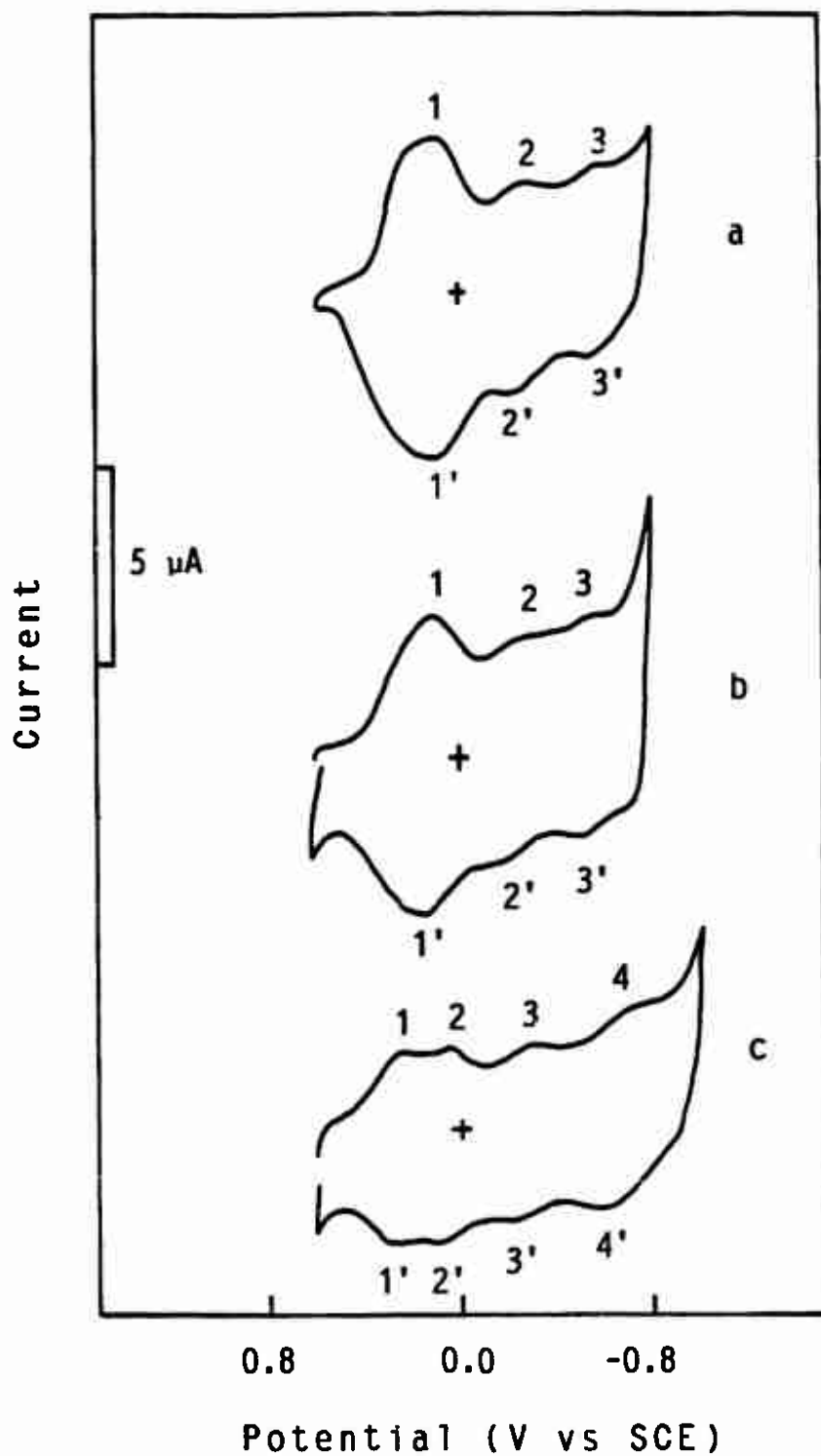


Figure 7. Cyclic Voltammograms of PMePc film electrodes.  
(a) PNiPc, (b) PCuPc, (c) PCoPc

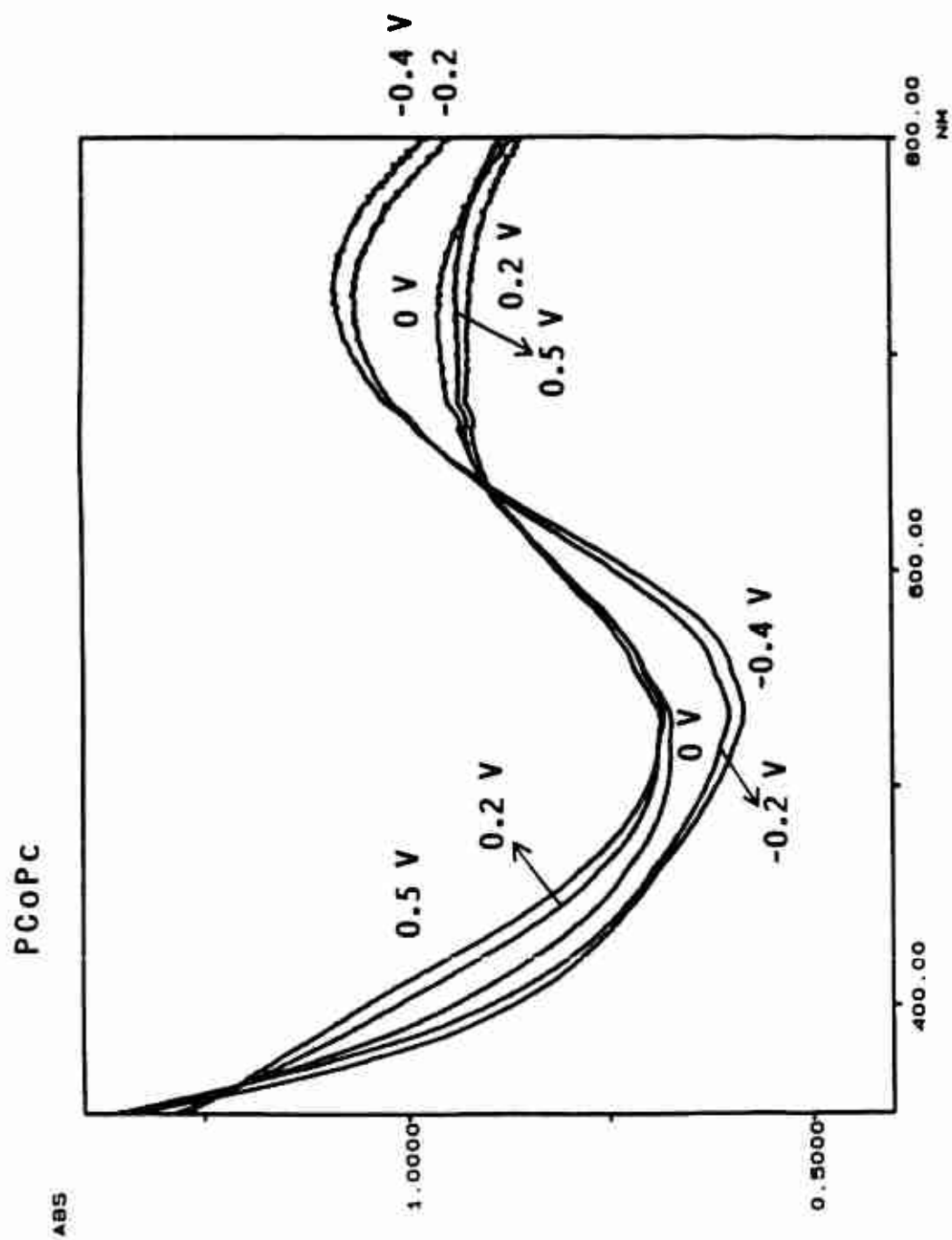


Figure 8A. In-situ UV-visible spectra of PCoPC thin film.  
Potential range: 0.5 - -0.4 V.

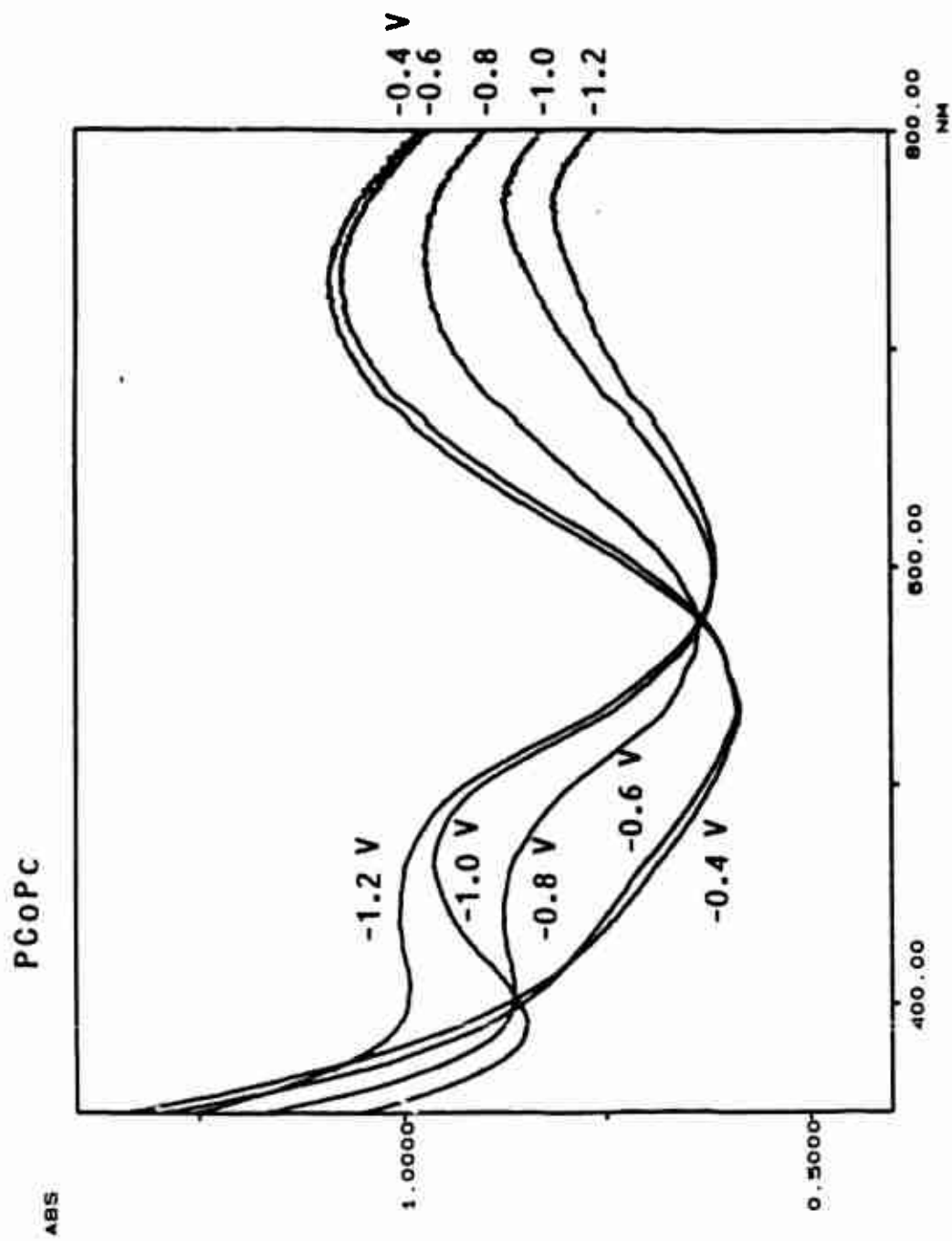


Figure 8B. In-situ UV-visible spectra of PCoPC thin film.  
Potential range: -0.4 - -1.2 V.

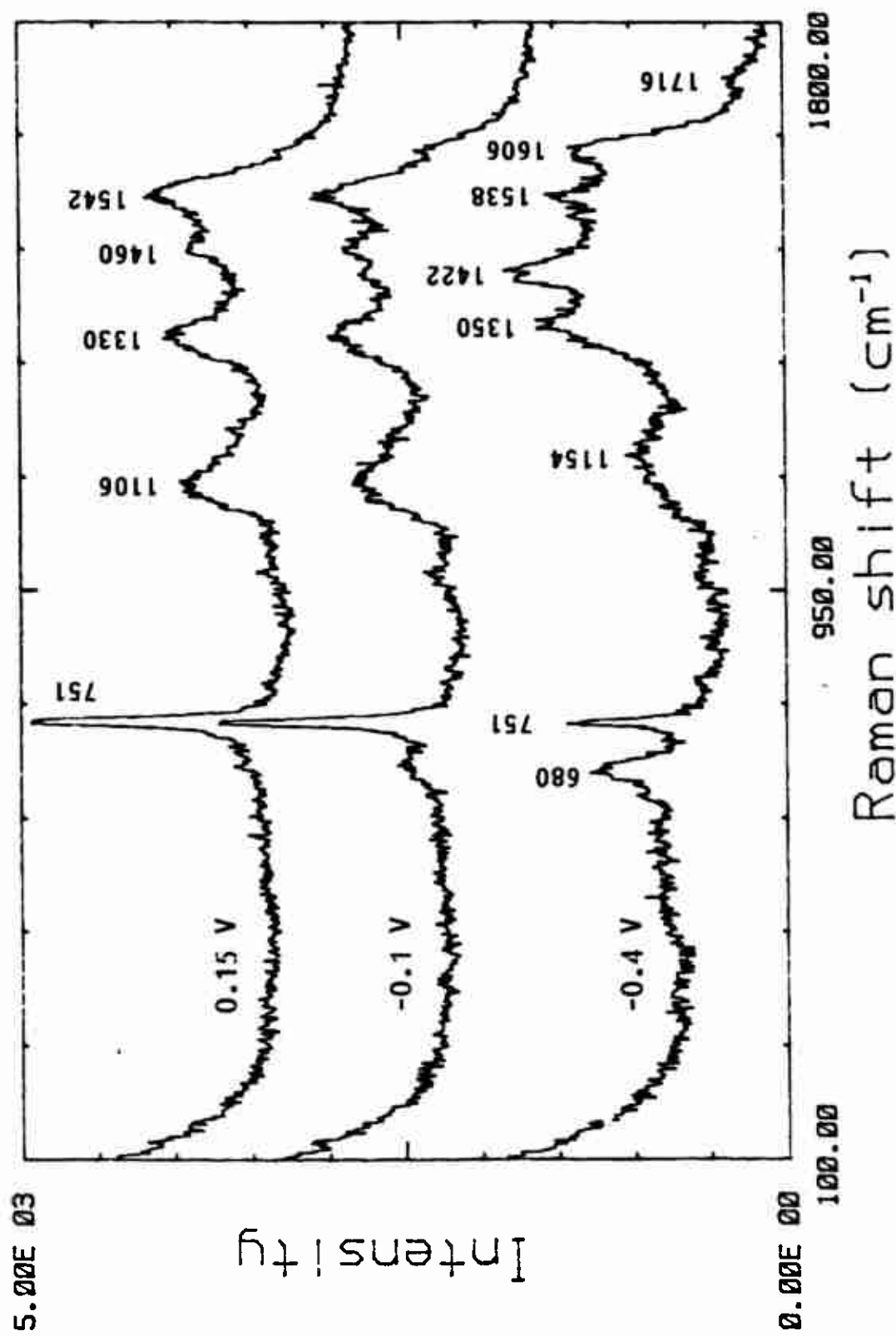


Figure 9. In-situ Raman spectra of PCoPc film in air saturated PB solution.